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|---|-------------------|------------------|
| Last Name | First Name | MI |
| Student ID Number : | | Signature |
| Name of your TA: (Please Circle) Bree / Eric | | Total: |
| Discussion Section - Day : Time: | | / 200 |

**Chem 30 A Winter 2008
Final
(180 mins)
Wednesday
March 19, 2008**

| | | | | | | |
|-----------|-----------|-----------|-----------|-----------|-----------|----|
| | | | | H | | He |
| Be 1.5 | B | C | N | O | F | Ne |
| Mg 1.2 | Al 1.5 | Si 1.8 | P 2.1 | S 2.5 | Cl 3.0 | Ar |
| Ca 1.0 | Ga 1.6 | Ge 1.8 | As 2.0 | Se 2.4 | Br 2.8 | Kr |
| Sr 1.0 | In 1.7 | Sn 1.8 | Sb 1.9 | Te 2.1 | I 2.5 | Xe |

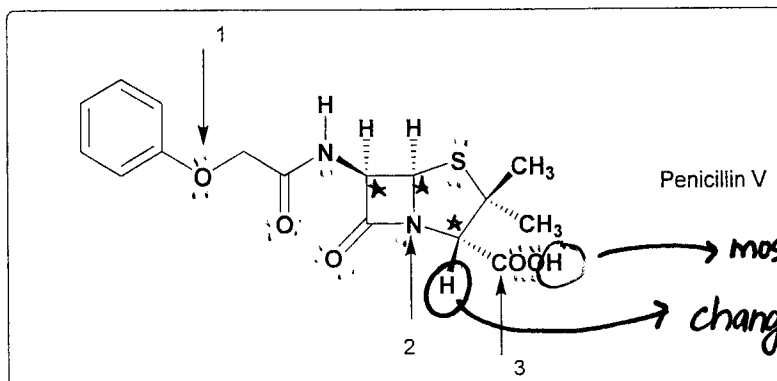
Electronegativity values for some atoms
(Pauling scale)

DO NOT OPEN THIS EXAM UNTIL INSTRUCTED TO DO SO

| | Page | Point | Score |
|----------|----------|-------|-------|
| Bree - [| 3 | 16 | |
| | 4 | 10 | |
| | 5 | 10 | |
| | 6 | 14 | |
| Eric - [| 7 | 12 | |
| | 8 | 15 | |
| | 9 | 14 | |
| | 10 | 18 | |
| Bree - [| 11 | 8 | |
| | subtotal | 117 | |

| | Page | Point | Score |
|----------|-------|-------|-------|
| L | 12 | 8 | |
| | 13 | 9 | |
| | 14 | 12 | |
| Erie - [| 15 | 10 | |
| | 16 | 10 | |
| | 17 | 10 | |
| | 18 | 10 | |
| | 19 | 8 | |
| Bree - [| 20 | 6 | |
| | Total | 200 | |

1. Penicillin V is a broad-spectrum antibiotic isolated from penicillium mold. Answer the questions below. (16 points)



- a. [2 points] What is the hybridization state of atoms (labeled 1, 2, and 3) in the Penicillin V?
- (a) ~~1.~~ sp 2. sp² 3. sp³ (b) 1. sp³ 2. sp 3. sp
- (c) 1. sp³ 2. sp³ 3. sp² (d) ~~1.~~ sp² 2. sp 3. sp²

C

 2pts

- b. [2 points] How many chiral centers are present in Penicillin V?

Answer is: 3

2pts

- c. [2 points] Identify the chirality centers by * on the above structure.

2pts

- d. [2 points] How many lone pairs of electrons are present in Penicillin V?

Answer is: 14

2pts

- e. [4 points] Name all the functional groups present in Penicillin V? (use primary / secondary where appropriate)

Answer: ether, amide, sulfide, carboxylic acid

4pts

- f. [2 points] Identify the most acidic proton in Penicillin V (Circle the proton on the above structure)?

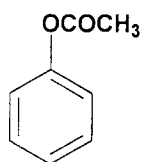
2pts

- g. [2 points] Indicate one transformation that you will make to synthesize a new analog of penicillin V that is more acidic than the present molecule? Explain in less than 15 words.

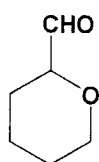
- change COOH to COSH
- change α -H to halogen (F)

2pts

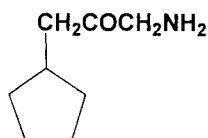
2. [2 points] Which structures belong to the ester class of molecules?



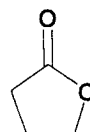
I



II



III



IV

(a) I and II

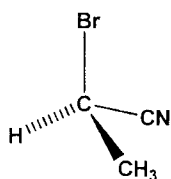
(b) III only

(c) IV only

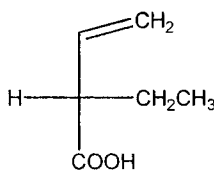
(d) I and IV

d 2pts

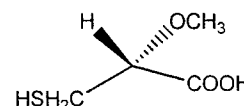
3. [6 points] What are the configurations for the stereocenters in the given molecules?



I



II



III

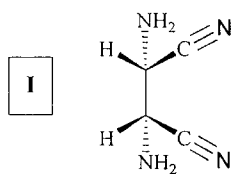
2pts each

R

S

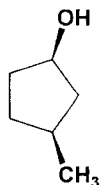
R

4. [2 points] Which are meso compounds?

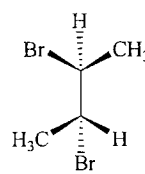


I

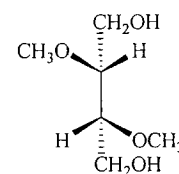
II



III



IV



(a) I

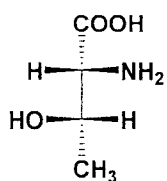
(b) II, III

(c) III, IV

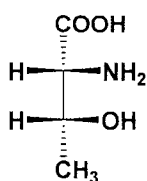
(d) I, III

d 2pts

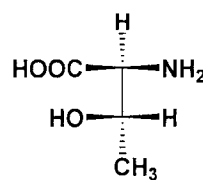
9. [8 points] Stereoisomers of 2-amino-3-hydroxybutanoic acid (Threonine) are shown below:



I



II



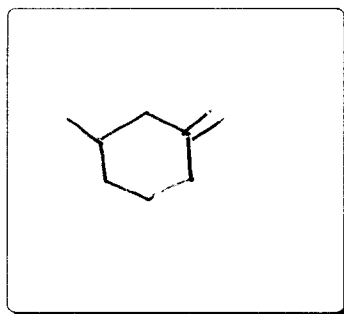
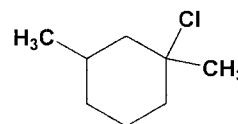
III

- a) [2 points] What is the relationship between structure I and II: diastereomers 2pt
- b) [2 points] What is the relationship between structure II and III: enantiomers 2pt
- c) [4 points] Which structure represents the (2R,3R) isomer: II 4pt

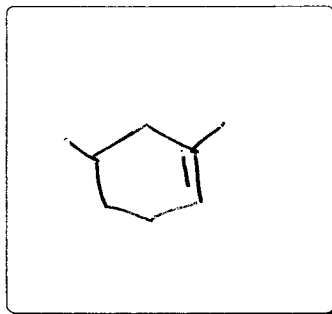
10. [6 points] Draw 3 isomeric compounds (I; II; III) which when treated with HCl give the product in the reaction shown below?

I / II / III

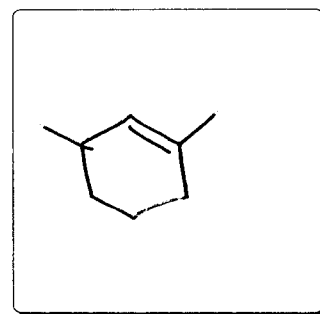
HCl



I



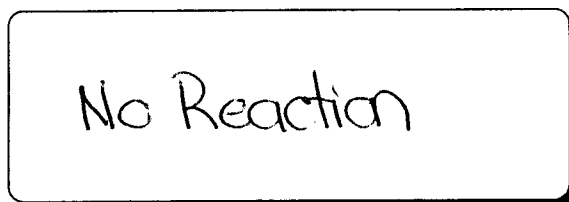
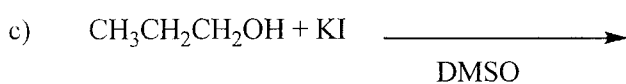
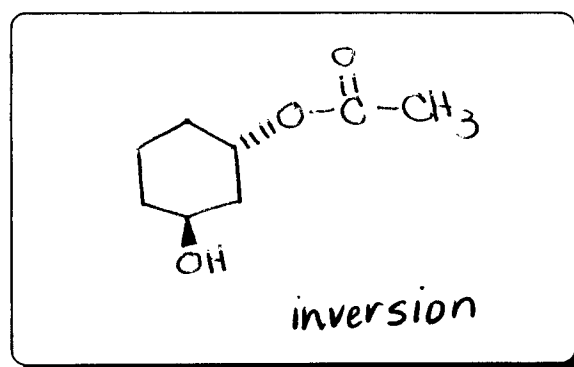
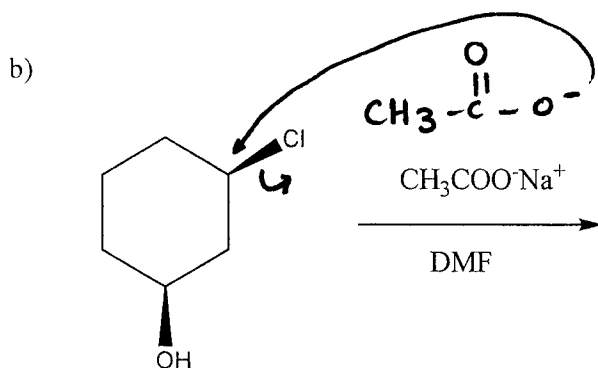
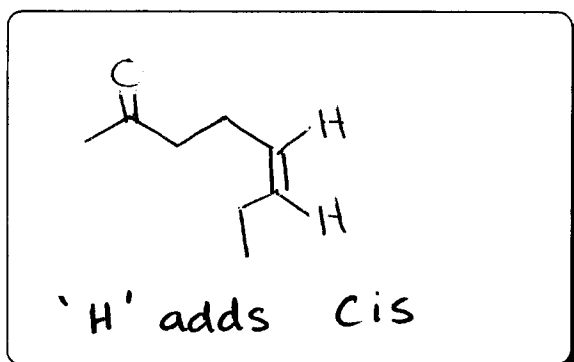
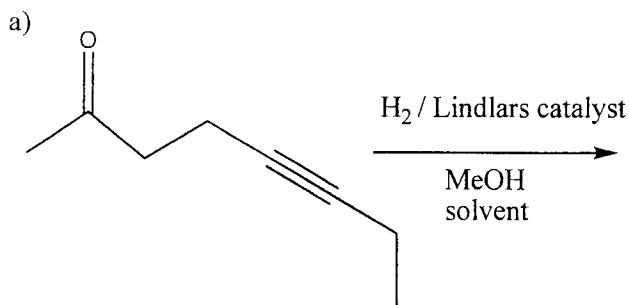
II



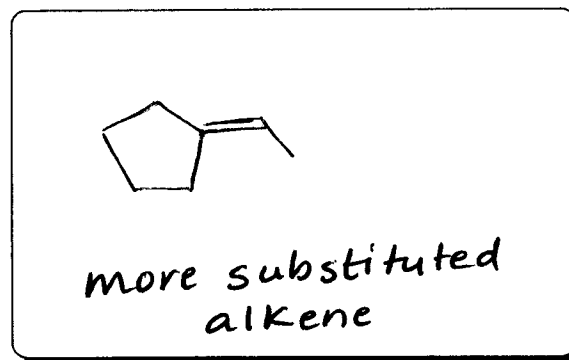
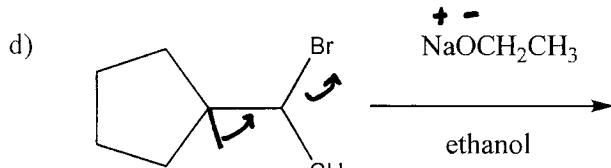
III

2pts
each

11. [3 points each] Give the major product of the following reactions. Show stereochemistry and all possible stereoisomers where appropriate. Write "No Reaction" where appropriate.

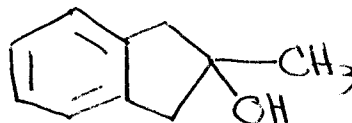
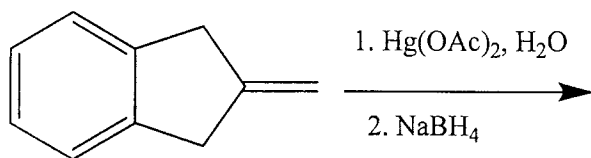


OH is not a leaving group



B: H^+
Leaving group on
 2°C & base (RO^-)
 \therefore Eliminated

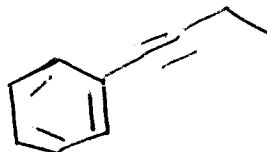
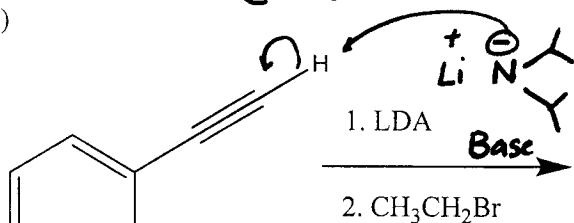
e)



3pts

(hydration)

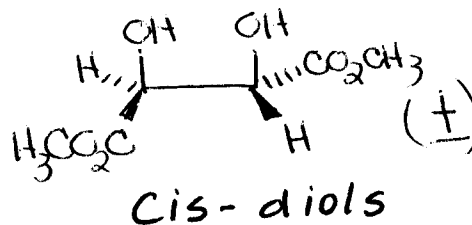
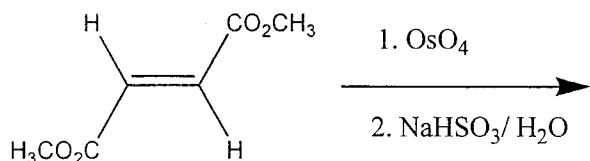
f)



3pts

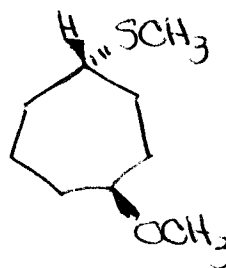
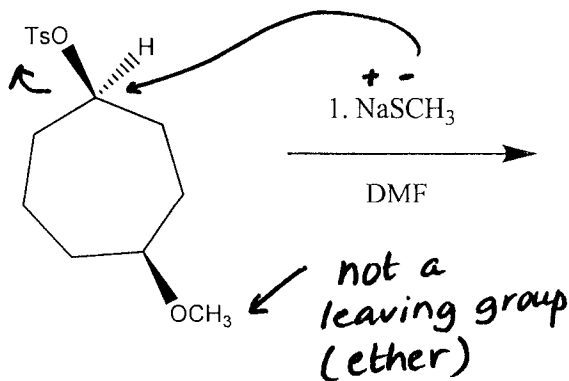
(Alkylation)

g)



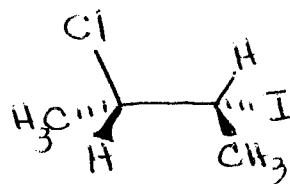
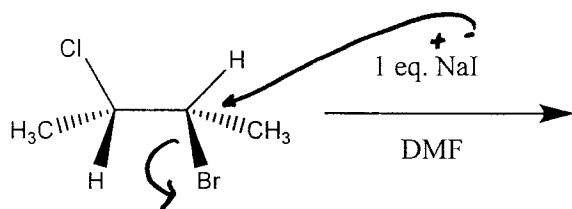
3pts

h)



3pts

i)



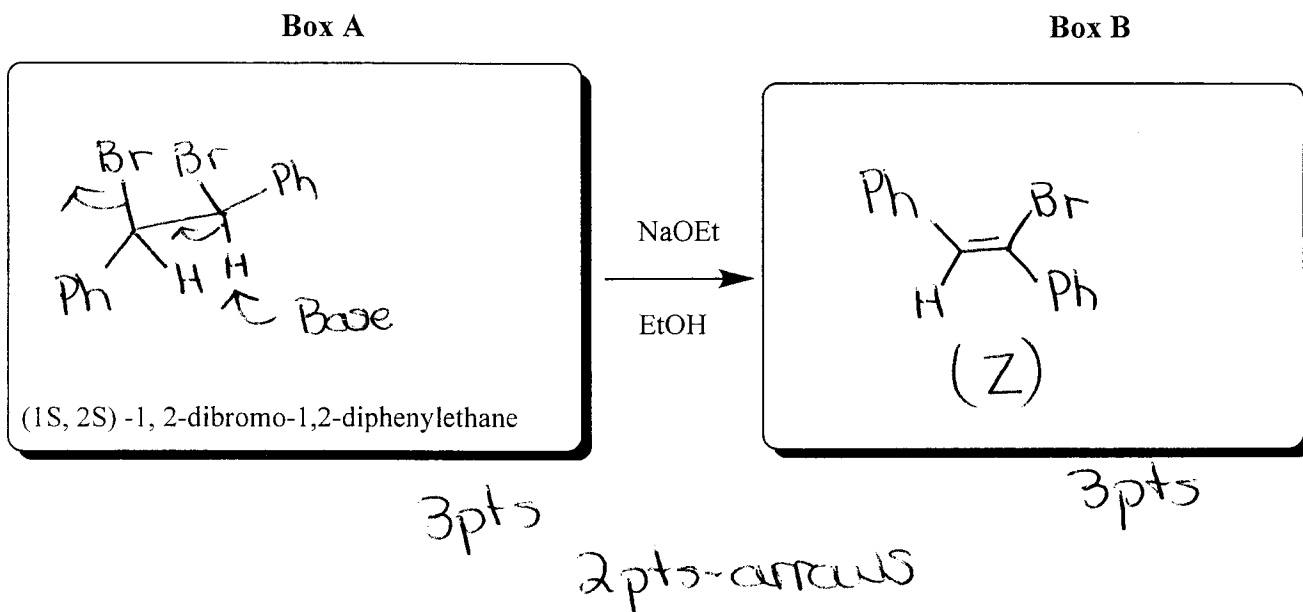
3pts

Br^- is a better leaving group than Cl^-

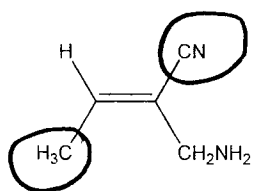
12. [8 points] What stereochemistry do you expect for the alkene obtained by E-2 elimination of (1S, 2S) -1,2-dibromo-1,2-diphenylethane.

Draw the sawhorse formula of (1S,2S) -1, 2-dibromo-1,2-diphenylethane (Box A) and the alkene product in Box B.

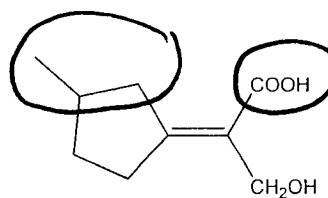
Show proper arrows to demonstrate the E-2 elimination.



13. [6 points] Designate the following alkenes as **E** or **Z**. (Place the letter in the box). **CIRCLE** the highest priority groups on each of the sp^2 carbons.



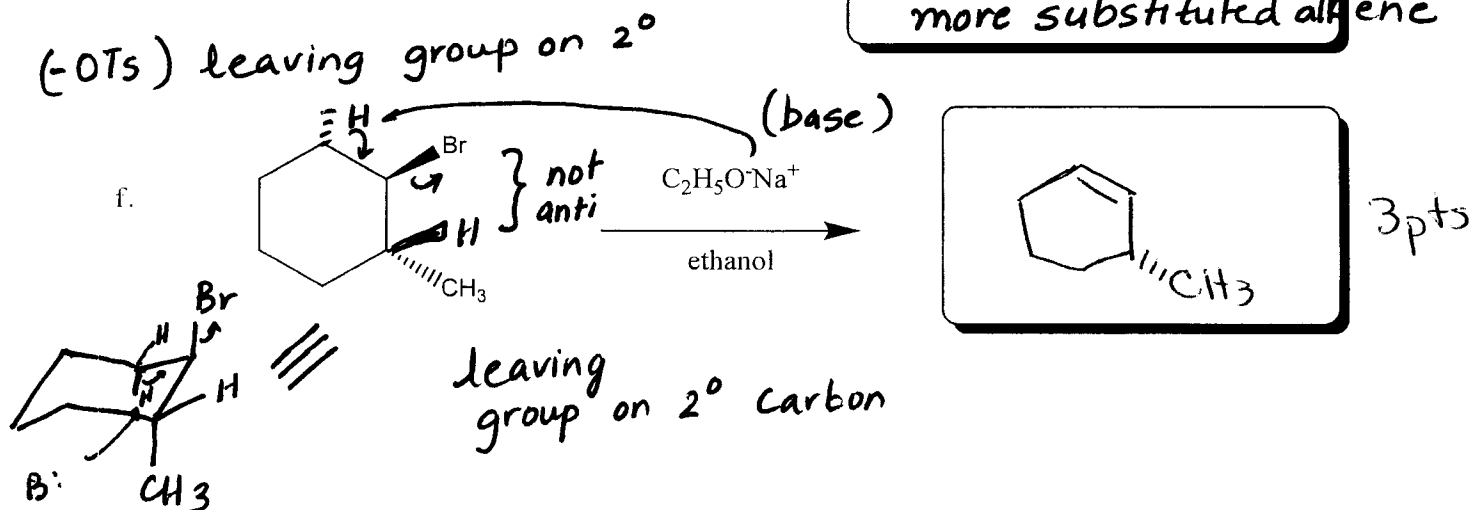
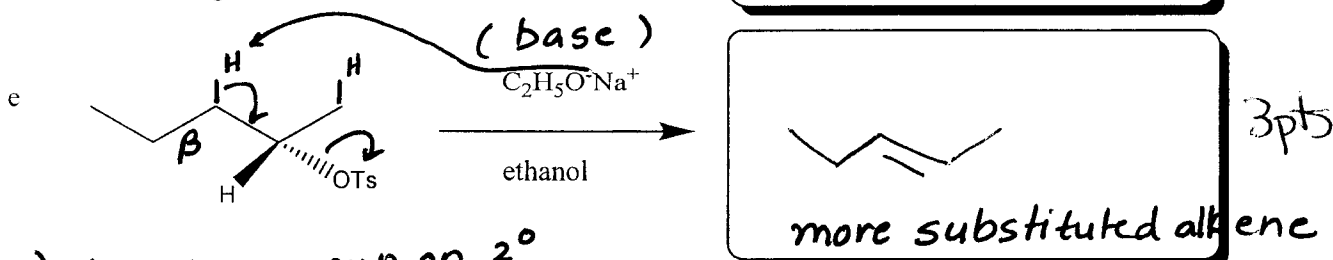
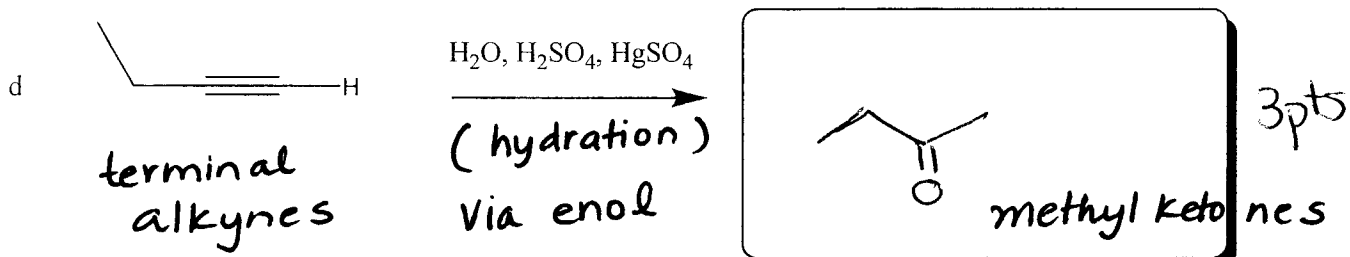
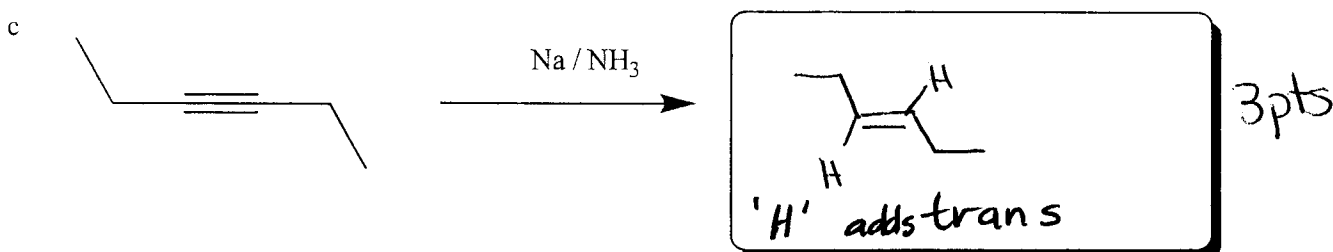
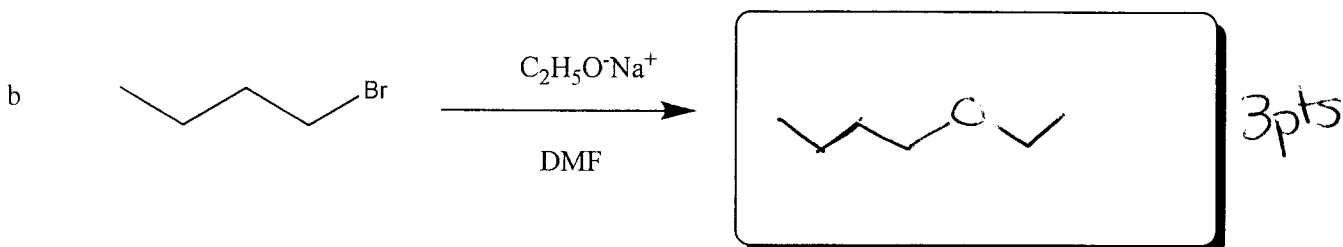
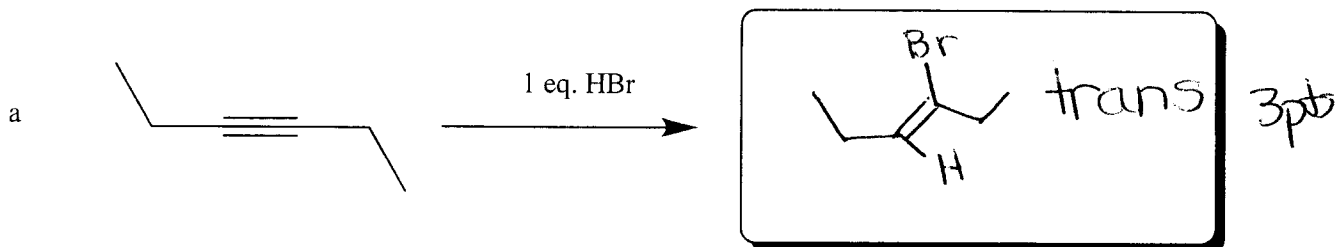
E



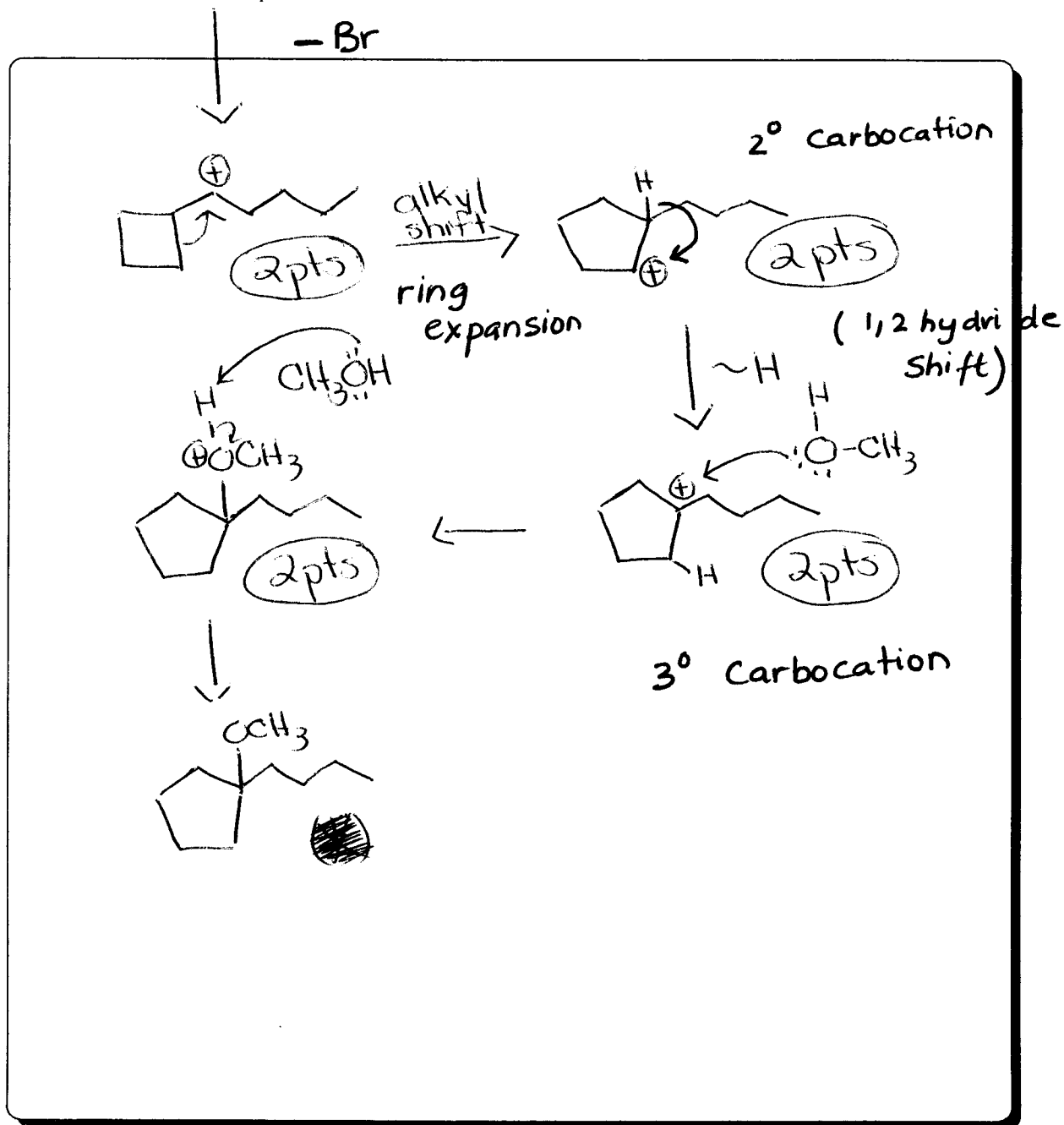
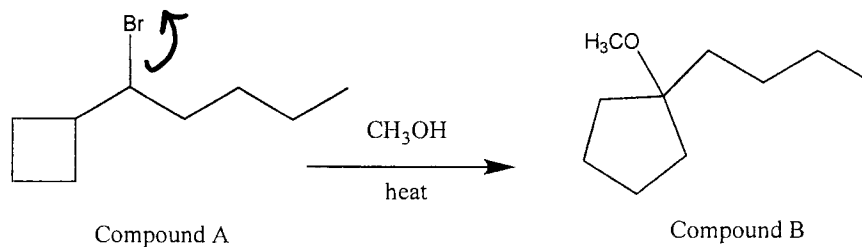
Z

3pts each

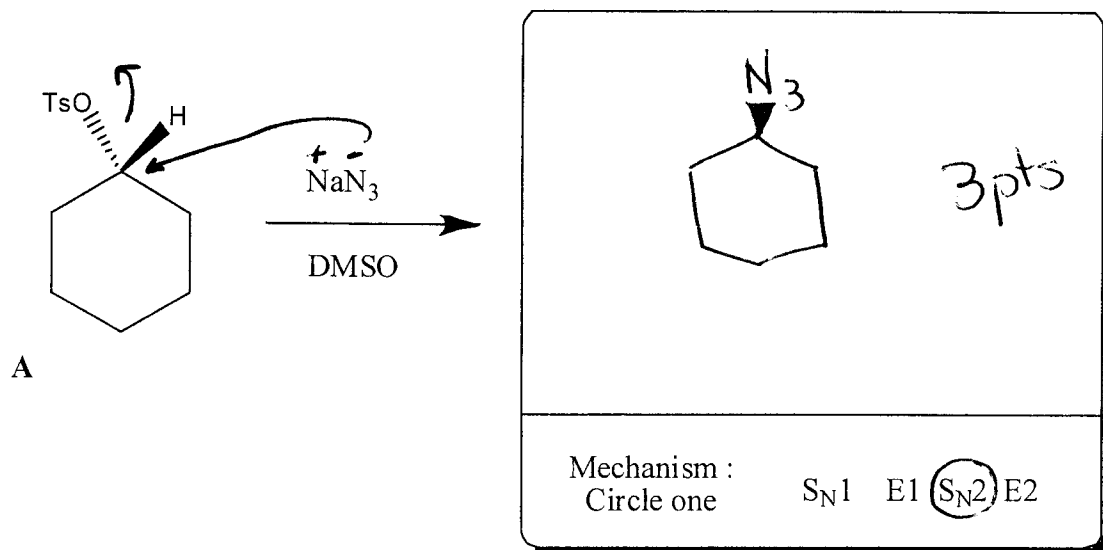
14. [18 points] Give the major product of the following reactions. Please indicate stereochemistry where ever possible.



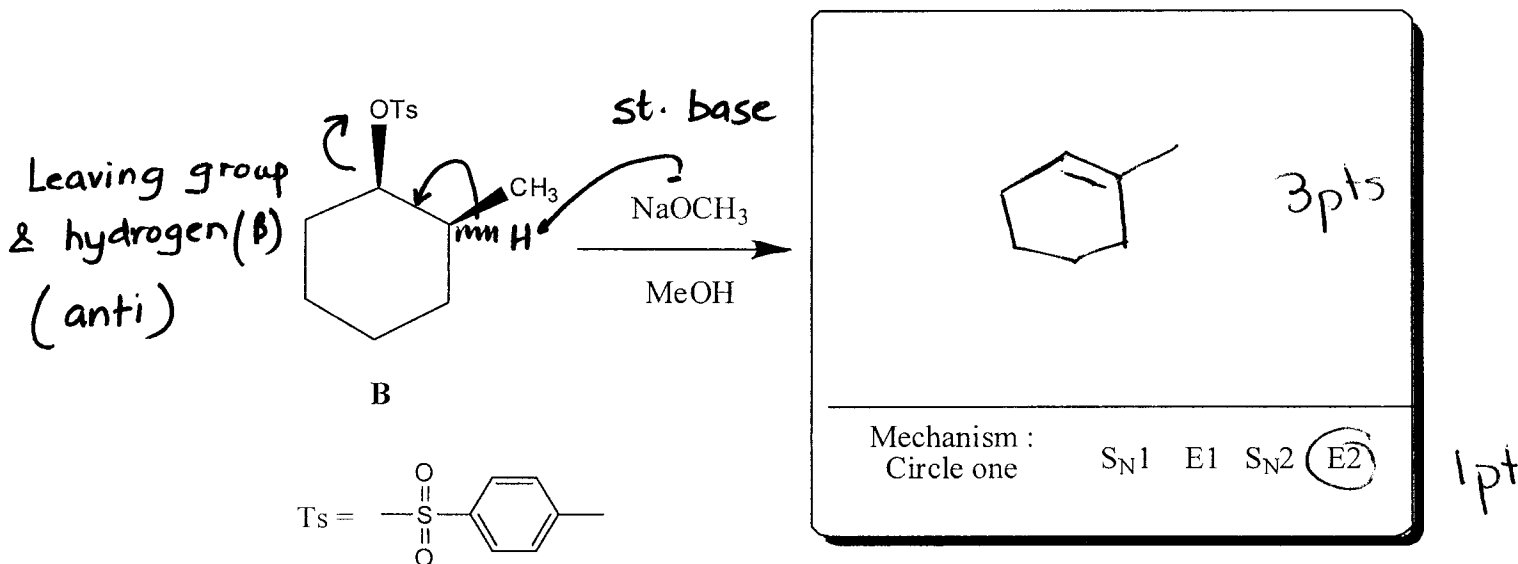
15. [8 points] Provide a reasonable mechanism to account for the transformation (solvolysis) of A into B— show all steps including the properly drawn curved arrows and all intermediates. Make sure each individual step is mass- and charge-balanced.



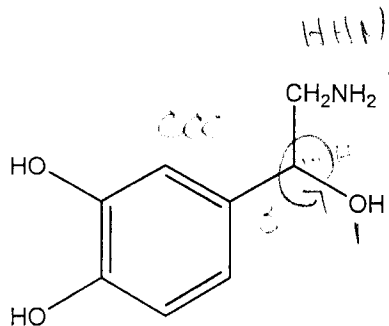
- 16.(a) [4 points] Write the product of the reaction of tosylate A with sodium azide in DMSO. Provide stereochemistry if applicable.



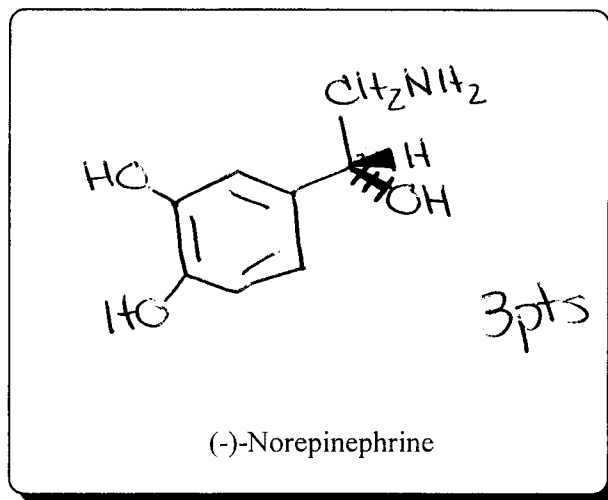
- 16.(b) [4 points] Write the major product for the reaction of tosylate B with sodium methoxide in MeOH. Provide stereochemistry if applicable.



17. [3 + 2 points] Norepinephrine is a biologically important molecule. (-)-Norepinephrine is the (R) isomer and has the required physiological property as a hormone and a neurotransmitter. Draw the 3-D structure of (-)-Norepinephrine.



Norepinephrine



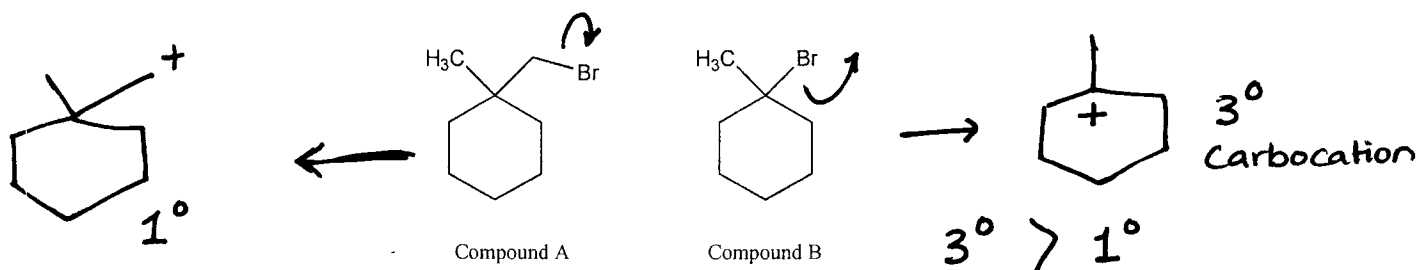
(-)-Norepinephrine

What can you say about the biological property of the S isomer? Explain in less than 15 words.

it may have totally different properties
∴ binding to chiral receptors in a different way

2pts

18. [4 points] Compound A is stable in ethanol ($\text{CH}_3\text{CH}_2\text{OH}$), B is rapidly converted to another compound. Explain (less than 25 words)



Compound B is a tertiary alkyl halide and is susceptible to $\text{S}_{\text{N}}1$ attack by MeOH , whereas Compound A is a 1° alkyl halide and will not undergo $\text{S}_{\text{N}}1$ attack so it is stable in MeOH .

4pts

19. [4 + 3 points] A hydrocarbon of unknown structure has the formula C_8H_{10} . On catalytic hydrogenation over Lindlar catalyst, 1 equivalent of H_2 is absorbed. On hydrogenation over a Palladium catalyst, 3 equivalents of hydrogen are absorbed.

a) How many degrees of unsaturation are present in the unknown?

Answer is: 4

1 pt

b) How many triple bonds are present?

Answer is: 1

1 pt

c) How many double bonds are present?

Answer is: 2

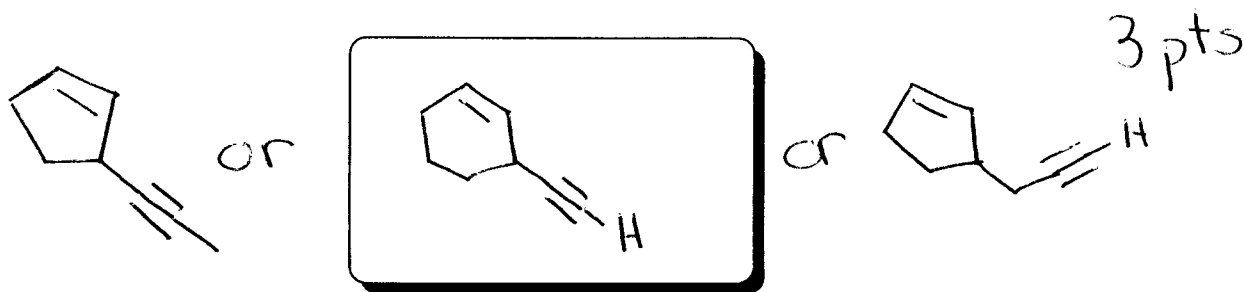
1 pt

d) How many rings are present?

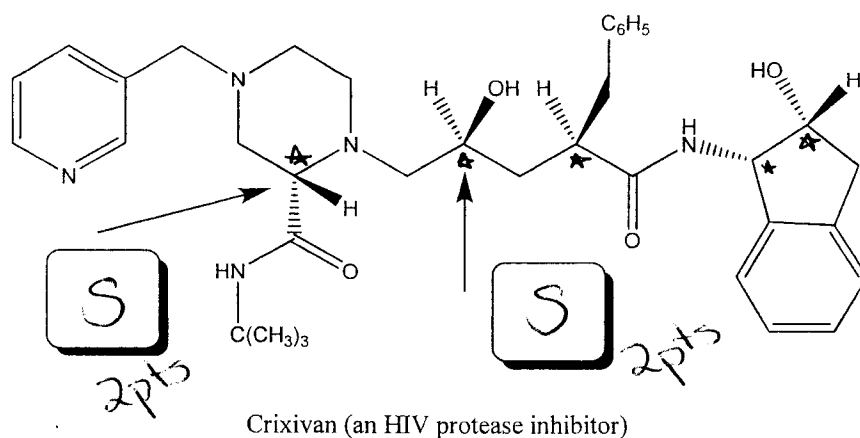
Answer is: 1

1 pt

e) Draw one structure that fits the data?



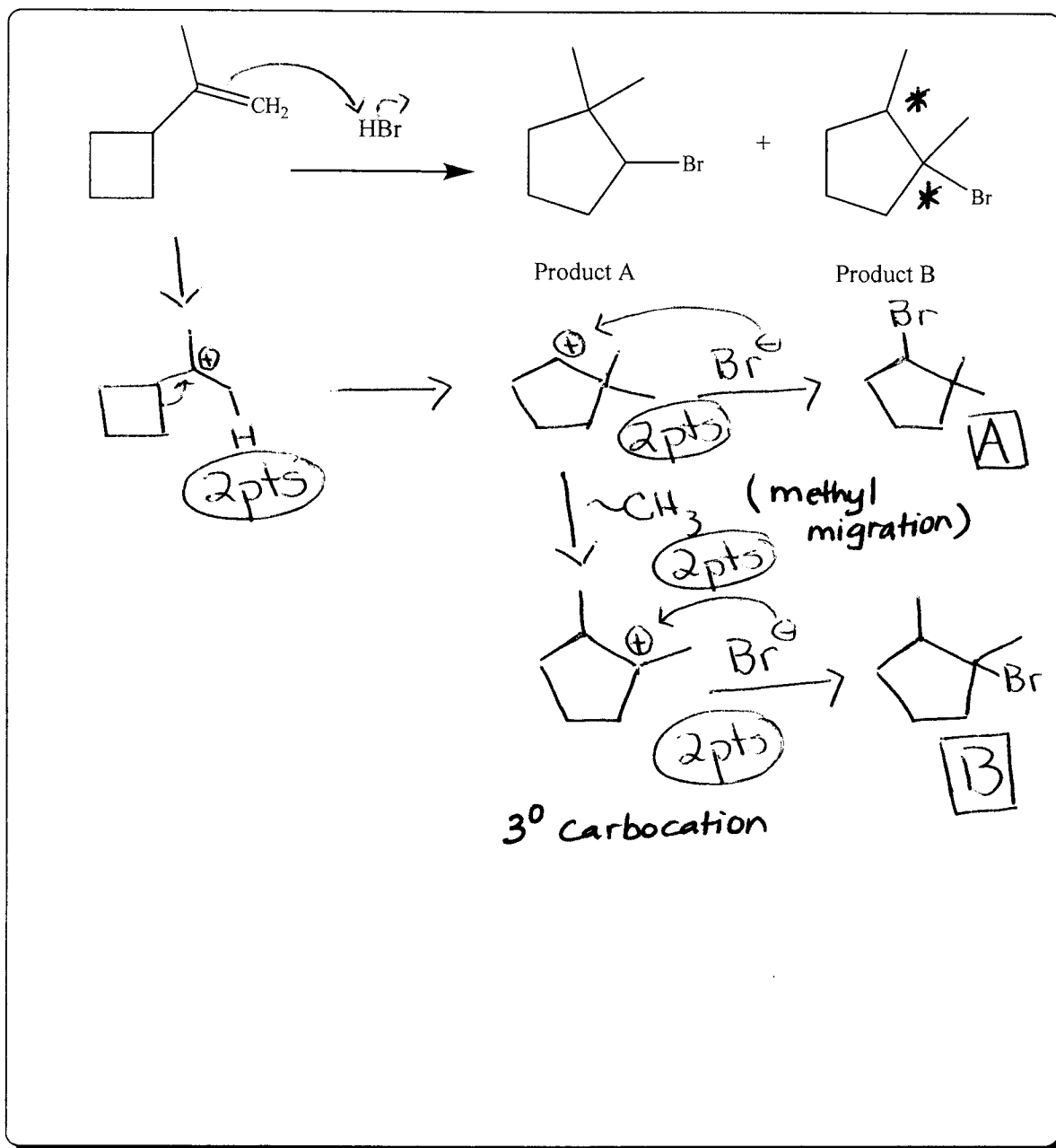
20. [5 points] Give the absolute configuration of the stereocenters indicated by the arrow in the molecule called "Crixivan".



How many stereoisomers are possible for Crixivan? 2⁵ 1 pt

21. [10 points]

(a) Propose a mechanism for the formation of **Product A** and **Product B**.

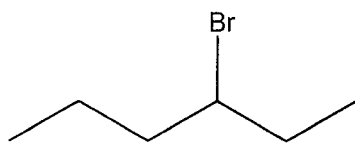


Which compound is the Major Product and why? B b/c via 3° carbocation

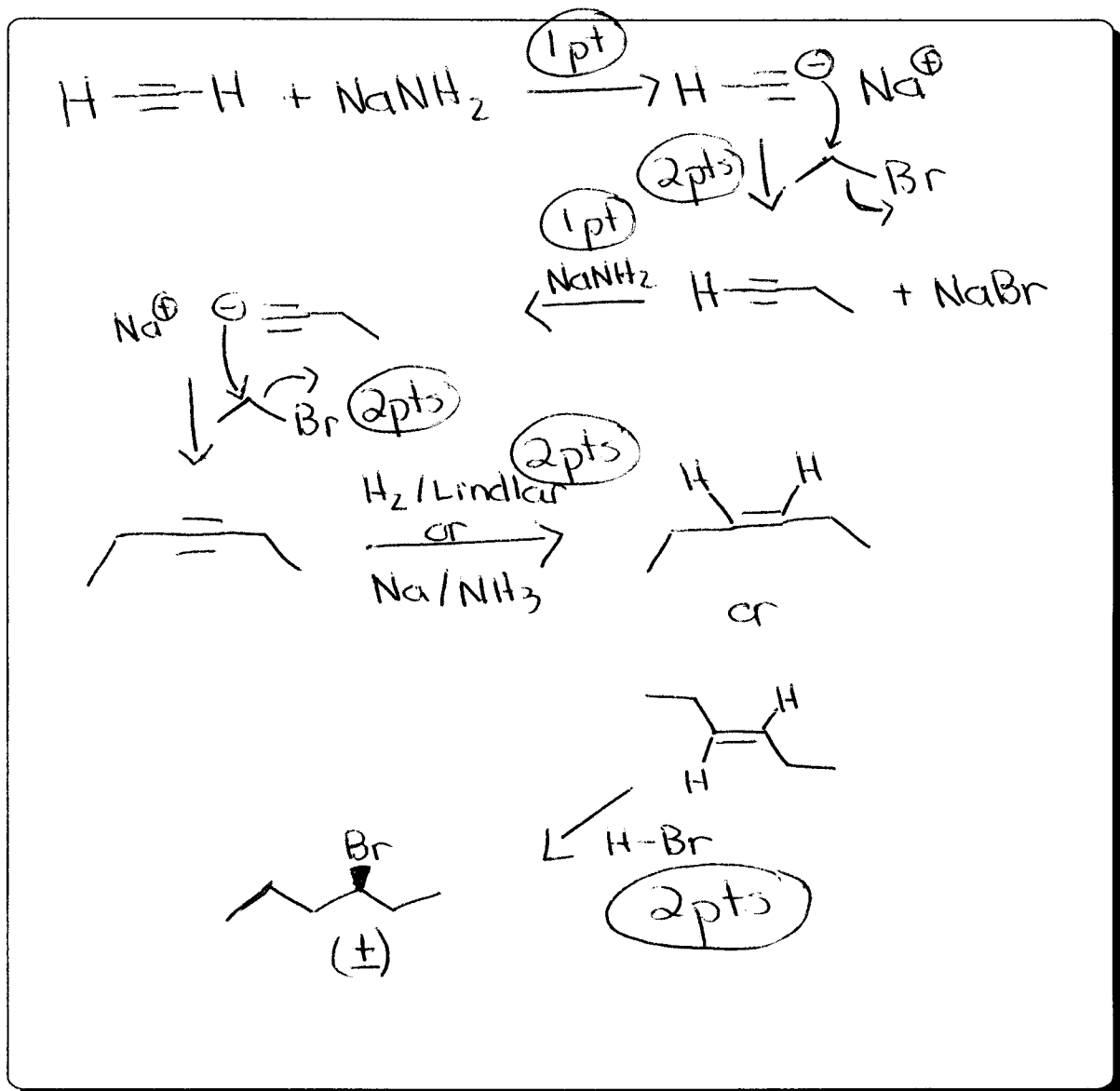
Product B will have 2² stereoisomers.

2pts

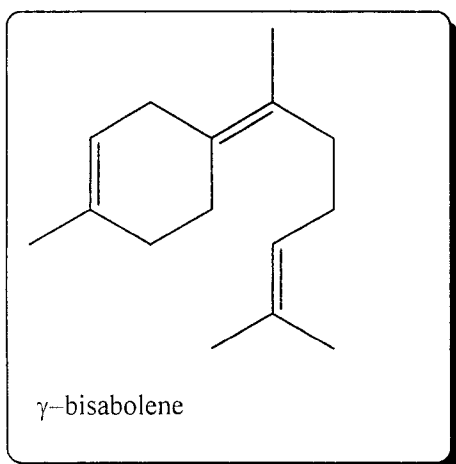
22. [10 points] Synthesize 3-bromohexane from acetylene (a two carbon alkyne) and appropriate alkyl halide (will require more than 1 step). Show stepwise synthesis and provide the reagents that you will use for the transformation.



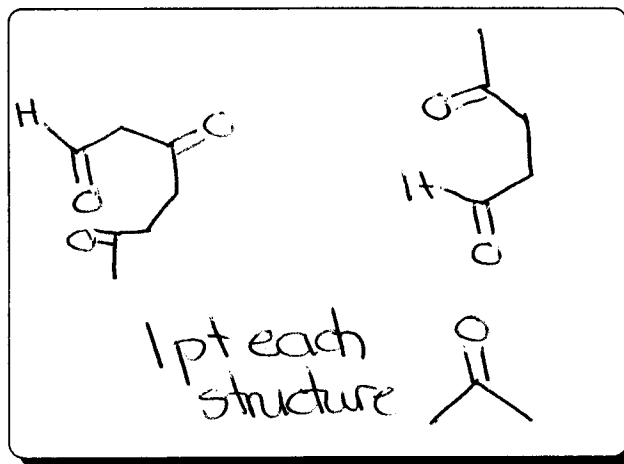
Compound A



23. [10 points] Predict the Ozonolysis products for the terpenes shown below.



1. O_3
2. $(CH_3)_2S$



How many chiral centers are present in γ -bisabolene?

0

1pt

How many Cis double bonds are present in γ -bisabolene?

1

1pt

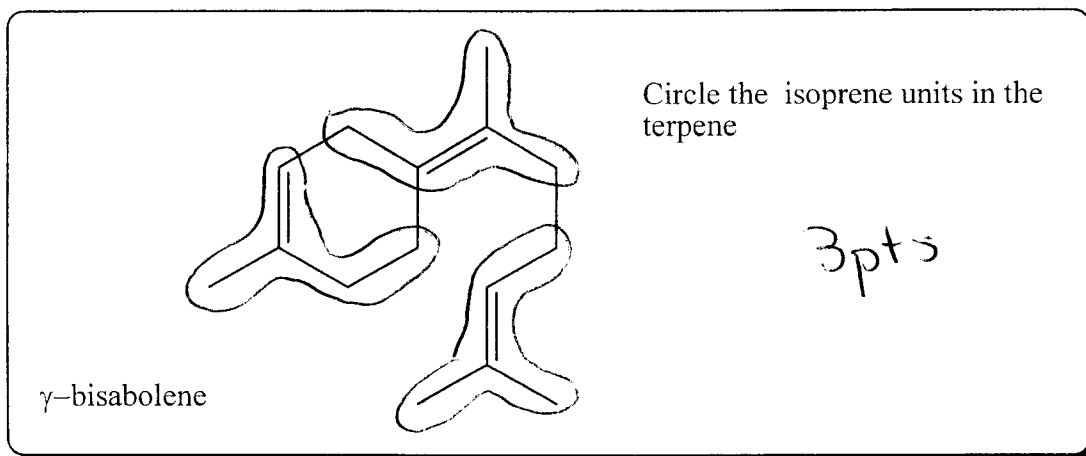
How many stereoisomers can γ -bisabolene have?

2

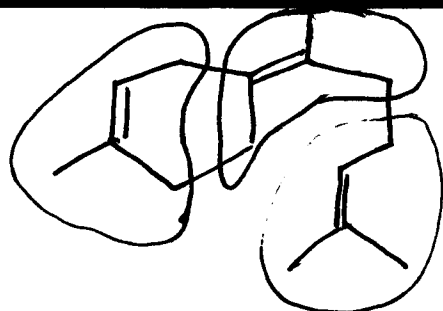
1pt

γ -bisabolene is made up of 3 isoprene units.

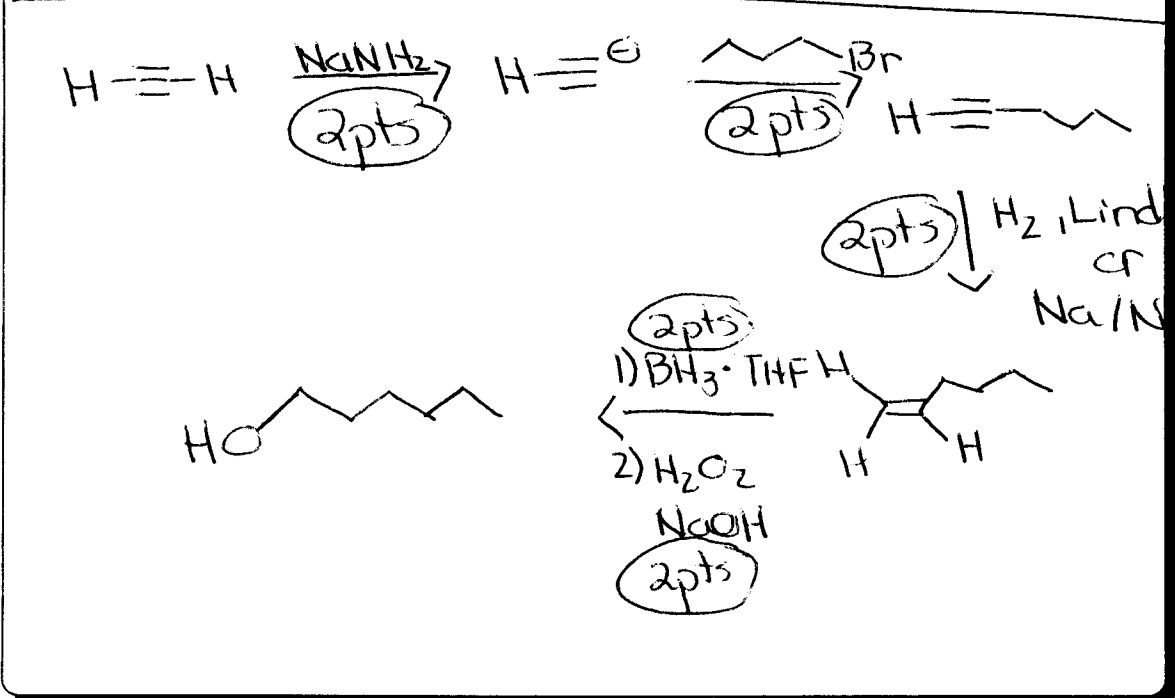
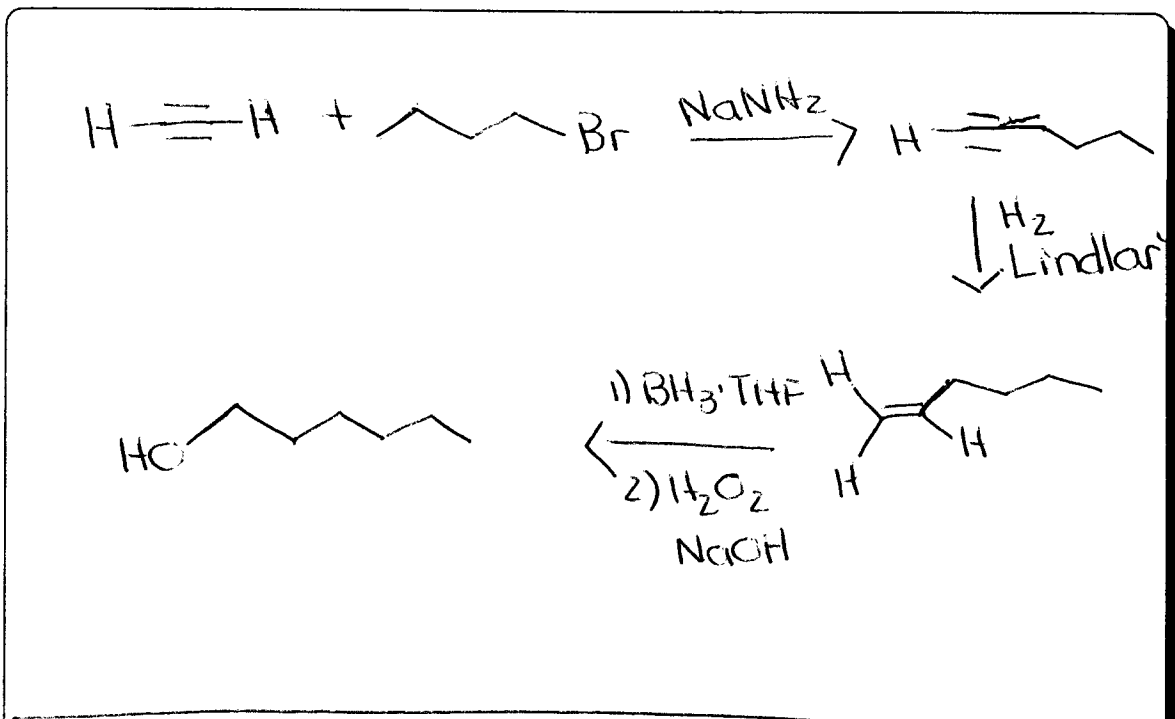
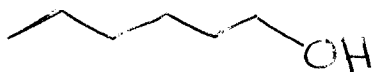
1pt



OR



24. [10 points] Synthesize 1-hexanol beginning from acetylene (two carbon alkyne; C_2H_2) and an appropriate alkyl halide.



25. [8 points] Describe using Valence Bond Theory the orbitals used in bonding for Acetic acid [CH₃COOH]. Show ground state C and O, excited state electronic configuration state for C and hybridization of atomic orbitals for C and O and their overlap using proper orbital diagram. Using VSEPR predict the bond angles and geometry (shape) around the OCO bond.

4 pts
structure

2 pts

C: $1s^2 2s^2 2p^2$

| | | | |
|----|---|---|---------|
| ↑↓ | ↑ | ↑ | g.s. |
| ↑ | ↑ | ↑ | excited |

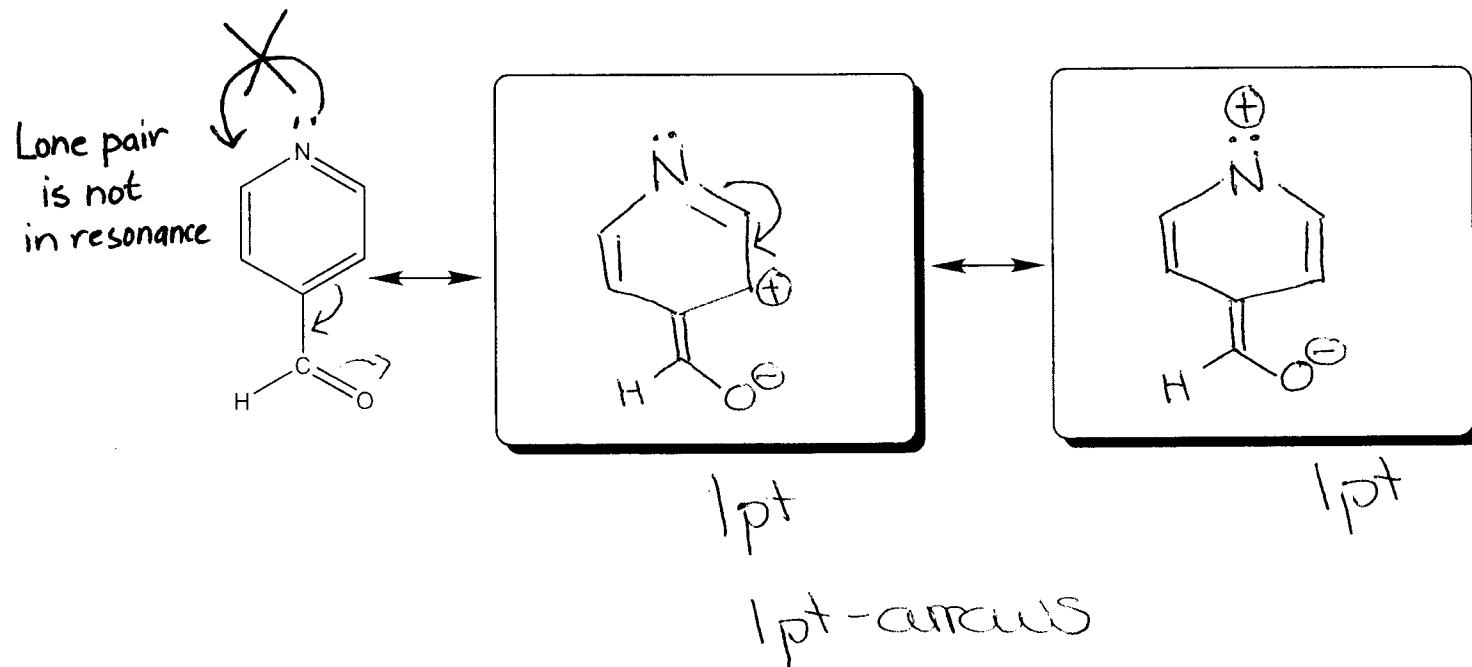
O: $1s^2 2s^2 2p^4$

| | | | | |
|----|----|---|---|------|
| ↑↓ | ↑↓ | ↑ | ↑ | g.s. |
|----|----|---|---|------|

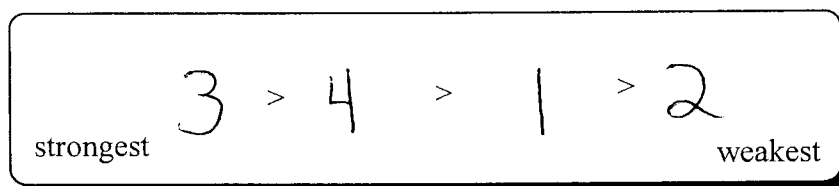
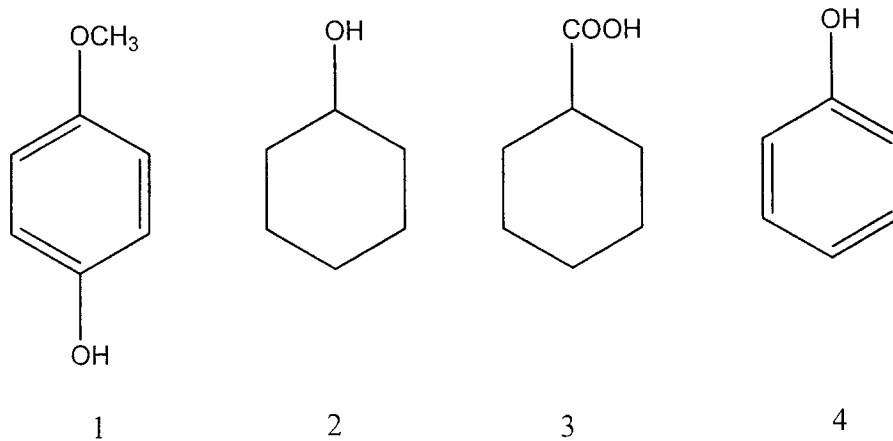
1 pt OCO Bond angle: 120°

1 pt Hybridization of Carbonyl Carbon: sp²

26. [3 points] Draw two resonance contributors of the aldehyde shown below. Show curved arrows to indicate movement of electrons.



27. [3 points] Provide the correct order of the acidity of the following compounds in the box below:



3pts